

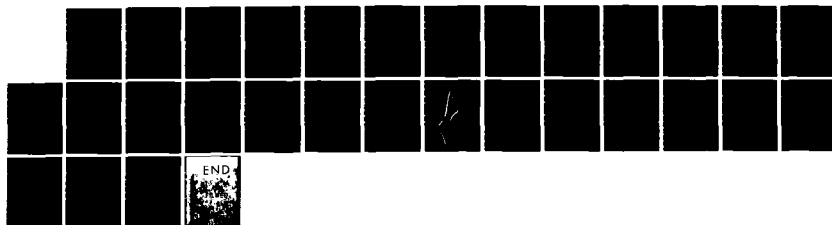
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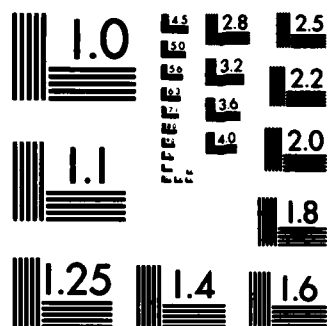
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20. ABSTRACT (continued)

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Effect of Hydrophobic Interactions on the Rates of  
Ionic Diffusion in Nafion Films at Electrode Surfaces

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### Summary

Results of studies of diffusional charge transport in films of 1100 and 1200 equivalent weight Nafion on glassy carbon electrode surfaces are reported. A comparison of apparent diffusion coefficients for the oxidized and reduced forms of various ionically diffusing redox couples shows that the ratio of these diffusion coefficients is critically dependent on the nature of the diffusing ion. For hydrophobic redox couples, the diffusion coefficient for the more highly charged form was always greater than the diffusion coefficient for the lower charge form (opposite of what is generally observed in aqueous solution). These results are interpreted in terms of the effect of hydrophobic interactions, with the polymer chain material, on the rate of ionic diffusion.

## Introduction

Considerable recent effort has been devoted to elucidation of the mechanisms of diffusional charge transport in films of a Nafion (1) polymer at electrode surfaces (2). A 970 equivalent weight (EW) version of this polymer was used in all of these studies. One of the more informative of these investigations (2a) centered on evaluation of the contributions of so-called electron hopping diffusion (2,3) (described by an electronic diffusion coefficient,  $D_{et}$ ) and true molecular or ionic diffusion (described by the ionic diffusion coefficient,  $D_o$ ) to the experimental (apparent) diffusion coefficient,  $D_{App}$ . The results obtained were interpreted in terms of Dahms' theory of "electronic conduction" in aqueous solutions (2,4), and three important results were reported (2a); these were: 1. Dahms' theory may be used to qualitatively predict the relative contributions of  $D_o$  and  $D_{et}$  to  $D_{App}$ . 2. Experimental diffusion coefficients associated with oxidation,  $D_{App}^{(n-1)+}$ , equal experimental diffusion coefficients associated with reduction,  $D_{App}^{n+}$ , for redox couples having  $D_{et}$  much greater than  $D_o$  (electron hopping diffusers). 3. For redox couples having  $D_o$  much greater than  $D_{et}$  (true ionic diffusers),  $D_{App}^{(n-1)+}$  is greater than  $D_{App}^{n+}$ , as it generally is for ionic diffusion in aqueous solution (2a).

We have recently reported a procedure for dissolving the commercially available EWs of the Nafion polymers (5). We have completed an extensive study of the mechanisms of diffusional charge transport in films of these higher (1100 and 1200) EW polymers at glassy carbon electrode surfaces. This study has corroborated 1 and 2 (above) but has shown that for ions for which  $D_o$  is much greater than  $D_{et}$ , the ratio  $D_{App}^{n+}/D_{App}^{(n-1)+}$  (the diffusion coefficient ratio) is critically dependent on the chemical characteristics of the diffusing ion (i.e.,  $D_{App}^{(n-1)+}$  is not always greater than  $D_{App}^{n+}$ ). These results are interpreted in terms of the effect of hydrophobic



interactions on the rate of diffusion in Nafion films. We report the results of this study and of related studies concerning transport characteristics of the 1100 and 1200 EW Nafion films at this time.

### Experimental

Materials. Samples of 1100 and 1200 EW Nafion were kindly donated by E. I. DuPont de Nemours and Co. Solutions of these polymers (0.6 wt./vol.%) were prepared using the procedure of Martin et al. (5). Glassy carbon rods (1/8 in. dia.) were obtained from Atomergic Chemetals Co. 1,1'-dimethyl-4,4'-bipyridinium dichloride, methyl viologen (the cations are referred to as  $MV^{2+}$  and  $MV^+$ ) was obtained from Aldrich and used without further purification.  $Fe(bpy)_3(ClO_4)_2$  ( $bpy=2,2'$ -bipyridine) and  $Fe(o-phen)_3(ClO_4)_2$  ( $o-phen=1,10$ -phenanthroline) were obtained from G. F. Smith and used without further purification.  $Ru(bpy)_3(ClO_4)_2$  was prepared from the dichloride (G. F. Smith) (6).  $Ru(NH_3)_6(PF_6)_3$  (7) and  $Co(bpy)_3(ClO_4)_2$  (8) were prepared by standard procedures. Ferrocenylmethyl trimethyl ammonium hexafluorophosphate (the cations are referred to as  $FA^+$  and  $FA^{2+}$ ) was prepared from the iodide salt (Pfaltz and Bauer) using aqueous  $NaPF_6$  and was recrystallized from water. A solution 0.2 M in trifluoroacetic acid (Sigma) having a  $pH=3.05\pm0.05$  was used throughout as the supporting electrolyte. All solutions were prepared with triply distilled water.

Electrode Preparation. The vitreous carbon rods were sanded flat with 600 grit silicon carbide paper and then polished with aqueous slurries of 1.0 then 0.3 and finally 0.05  $\mu M$  silica powder (Buehler). Buehler Texmet cloth was used to support the slurries. A Buehler III polisher/grinder with the Automet specimen rotator was used. Immediately after polishing, the electrodes were ultrasonically cleaned in 95% ethanol, rinsed with triply

distilled water and allowed to dry in air.

Nafion coating was accomplished by clamping a ca. 1 in. segment of rod in a chuck, so as to be perpendicular to the lab bench, and applying 1.5  $\mu\text{L}$  of a 0.6% solution to the pretreated surface. The films, therefore, contained  $1.03 \times 10^{-7}$  (1100 EW) and  $9.48 \times 10^{-8}$  (1200 EW) moles  $\text{cm}^{-2}$  of  $-\text{SO}_3^-$  sites. A five  $\mu\text{L}$  syringe with a flat-tipped needle was used to apply the polymer solutions. The solutions were applied in ca. 0.5  $\mu\text{L}$  increments and the syringe needle was used to spread each increment evenly across the electrode surface. The solvent (50:50 ethanol-water) was allowed to evaporate (ca. 10 min.) after which the rod was wrapped tightly with narrow strips of Teflon tape such that only the treated surface and about 1/8 in. of the opposite end were exposed. The rod was then sealed to the end of a glass tube using Teflon tape and a small quantity of Hg and a wire were inserted into the tube. The films were preconditioned for at least six hours (usually overnight) in supporting electrolyte before use.

Electrochemical Cell and Equipment. A standard three electrode cell using a Pt flag counter electrode and either a saturated calomel (SCE) or a saturated mercurous sulfate (SMSE) reference electrode was used. The SMSE was used only with  $\text{Ru}(\text{bpy})_3^{2+}$ . Electrochemical measurements were performed with a Princeton Applied Research Corp. model 175 programmer, model 173 potentiostat and model 179 digital coulometer. Either a Houston Instruments model 2000 X-Y recorder or a Nicolet 2090-3 digital oscilloscope was used to record cyclic voltammograms. Chronocoulometric transients were recorded using the Nicolet scope. All solutions were degassed with water saturated, prepurified  $\text{N}_2$  for at least 20 minutes before use. The solutions were blanketed with  $\text{N}_2$  during the electrochemical measurements.

Measurements. Films were loaded with the desired electroactive counterion by exposure to a solution of the ion in supporting electrolyte. The loading process was followed by cyclic voltammetry (2b). The quantity of electroactive ion loaded was determined coulometrically (2b). Unusual behavior was observed for  $\text{Co}(\text{bpy})_3^{3+/2+}$ . While "normal" (2) diffusional voltammograms were observed during loading (figure 1a) and in supporting electrolyte solution immediately after loading, after quantitative oxidation and re-reduction of the  $\text{Co}(\text{bpy})_3^{3+/2+}$  in the film, sharp anodic and cathodic spikes were observed in the voltammograms (figure 1b). The peak currents of these spikes increased with the number of quantitative oxidation/re-reduction cycles and, interestingly, so did the intercept in the chronocoulometric plots of  $Q$  vs.  $t^{1/2}$  (figure 2). This behavior may result from a morphological change in the polymer film in the vicinity of the polymer/substrate interface. It is of interest to note that this type of behavior was apparently not observed in the 970 EW films (2a) and that it was only observed here when  $\text{Co}(\text{bpy})_3^{3+/2+}$  was the diffusing ion. The slopes of the chronocoulometric plots did not change with oxidation and re-reduction (figure 2) and, therefore, reproducible values of  $D_{\text{App}}$  could be obtained.

Film thicknesses were calculated using  $1.58 \text{ g cm}^{-3}$  and  $1.66 \text{ g cm}^{-3}$  as the wet,  $\text{Na}^+$  form densities of the 1100 and 1200 EW polymers respectively (9). Film thicknesses of  $0.72 \text{ }\mu\text{m}$  (1100 EW) and  $0.68 \text{ }\mu\text{m}$  (1200 EW) were obtained. Apparent diffusion coefficients were determined from chronocoulometric plots of  $Q$  vs.  $t^{1/2}$  (2,10). These plots showed excellent linearity (correlation coefficients typically around 0.999) over time intervals where semi-infinite linear diffusion obtains (generally less than 400 ms). Typical plots are shown in figure 3. Slopes for several of the cations initially decreased with repetitive potential steps. This behavior has been observed for other polymer-based chemically modified electrodes (11) and possible causes have

been discussed by Chambers (11). Uncompensated film/solution resistance was evaluated as described by Martin et al. (12).  $D_{App}$  values obtained with compensation were not significantly different than those obtained without compensation (13). The data shown in Table I was obtained without compensation.

### Results and Discussion

Some of the chemical and electrochemical properties of thin films of the commercially available (1100 and 1200) EW Nafions have been reported by Martin et al (5). Films of these polymers show the same trends in solubility and ion exchange selectivity (5) as the well-characterized 970 EW Nafion. No study of the transport characteristics of thin films of the 1100 and 1200 EW polymers has, however, been reported. One of the first questions we wanted to address was how  $D_{App}$  values vary with EW. We have compared  $D_{App}$  values (both  $D_{App}^{n+}$  and  $D_{App}^{(n-1)+}$ ) for  $Ru(bpy)_3^{3+/2+}$ ,  $MV^{2+/+}$ ,  $Ru(NH_3)_6^{3+/2+}$  and  $Co(bpy)_3^{3+/2+}$  in 1100 EW films with values in 1200 EW films and have found no significant differences. This indicates that the less than 10% difference in EW between these two polymers does not substantially alter the morphological features of the films.  $D_{App}$  values for 1100 EW films are reported here.

Table I shows experimental film diffusion coefficients for various redox couples, the ratio  $D_{App}^{n+}/D_{App}^{(n-1)+}$  for each couple for film diffusional charge transport and  $D^{n+}/D^{(n-1)+}$  for several of the couples in aqueous solution ( $D$ =aqueous diffusion coefficient). It is first of interest to examine the diffusion coefficient ratio ( $D_{App}^{n+}/D_{App}^{(n-1)+}$ ) for the various couples. Dahms' theory (2a,4) would predict that the very large ions with very high values of the self-exchange rate constant (2a) (i.e.,  $Ru(bpy)_3^{3+/2+}$ ,  $Fe(o-phen)_3^{3+/2+}$  and  $Fe(bpy)_3^{3+/2+}$ ) would show predominately electron hopping diffusion. Accord-

ing to Buttry and Anson (2a),  $D_{App}^{n+}$  should equal  $D_{App}^{(n-1)+}$  for such couples\*, and this is indeed observed. On the other hand, because  $D_o$  would be expected to be larger for smaller diffusers, smaller ions may be in the realm where  $D_o$  is much greater than  $D_{et}$  (i.e., true ionic diffusers). For these ions  $D_{App}^{n+}$  would not be expected to equal  $D_{App}^{(n-1)+}$  (2a) and this is also observed in Table I. Hence, as noted in the introduction, this much more extensive study of diffusion in Nafion polymers has corroborated the first two conclusions suggested by Buttry and Anson's study (2a).

The third observation, that larger diffusion coefficients for the less highly charged ion of the redox couple ( $D_{App}^{(n-1)+} > D_{App}^{n+}$ ) may signal the dominance of true ionic diffusion (2a) was found, in this more extensive study, to be not universally true. While  $D_{App}^{n+}$  does not equal  $D_{App}^{(n-1)+}$ , for ions which might be predicted from Dahms' theory to be ionic diffusers, the value of the diffusion coefficient ratio is critically dependent on the nature of the diffusing ion. As was the case in the 970 EW films (2a),  $D_{App}^{n+}/D_{App}^{(n-1)+}$  for  $Ru(NH_3)_6^{3+/2+}$  is very close to the solution value (0.8) indicating that differences in the hydration energies for the  $n+$  and  $(n-1)+$  ions for this couple determine the magnitude of the film diffusion coefficient ratio (2a). However, diffusion coefficient ratios are much greater than the solution values for the other ions studied (Table I). This indicates that the decrease in hydration upon reduction of the  $n+$  ion in the film is more than compensated by an increase in some other interaction with the  $(n-1)+$ . This ancillary interaction is not present in aqueous solution.

\*Mathematical modeling of electron hopping diffusion makes the same prediction. (3b,c).

It is important to note that all of the couples which show large values of the film diffusion coefficient ratio are hydrophobic cations. It is well known that such cations can engage in strong hydrophobic interaction with, for example, the hydrocarbon interior of anionic micelles (14) and the hydrophobic parts of polyelectrolyte chains (15). Furthermore, there is a large body of evidence which suggests that strong hydrophobic interactions are possible between organic cations and the chain material in Nafion also. This evidence comes from ion-selective electrode selectivity data (16), fluorescence probing of Nafion films (17) and solutions (15b), and ion-exchange selectivity observed in electrochemical studies (2). In light of these studies, we propose that the large values of the diffusion coefficient ratios observed for hydrophobic cations here are caused by differences in the extents to which the  $n^+$  and the  $(n-1)^+$  ions engage in hydrophobic interactions with the fluorocarbon chain material. Because the  $(n-1)^+$  ions are more hydrophobic than the  $n^+$  ions, the  $(n-1)^+$  species engage in stronger hydrophobic interactions and their diffusion is less facile.  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  shows an aqueous-like diffusion coefficient ratio because both the  $n^+$  and the  $(n-1)^+$  ions are so hydrophilic that there are no hydrophobic interactions with either ion.

If this model for ionic diffusion is correct, the movement of ions through Nafion films is analogous to the movement of solute molecules through a reversed phase liquid chromatography (RPLC) column. In both cases, hydrophobic interactions with an immobile, nonpolar phase impede the progress of solute species through (film diffusion) or with (RPLC) a contacting, polar solution phase and in both cases, the speed with which the species reaches either the substrate (film diffusion) or detector (RPLC) depends on the strength of the hydrophobic interactions.

## Conclusions.

While the results obtained here clearly show that hydrophobic interactions can retard the rates of ionic diffusion in Nafion films, it is important to consider how these interactions arise. That is, a model for the cluster phase which accounts for the observed data is required. Yeager and Steck (18) and Rodmacq et al (19) have recently suggested that the ionic cluster in Nafion is biphasic. According to this model (18), an aqueous-like region, containing sulfonate exchange sites and the majority of the sorbed water (the ionic cluster) is surrounded by a region containing pendant side chains, some exchange sites and a smaller amount of water (the interfacial region). Yeager and Steck proposed this model to explain  $\text{Na}^+$  and  $\text{Cs}^+$  diffusion data in bulk Nafion membranes; the key point is that, because it is relatively hydrophobic,  $\text{Cs}^+$  partitions into the interfacial region where diffusion is hindered, while  $\text{Na}^+$ , which is very hydrophilic, remains in the aqueous cluster region where diffusion is much more facile.

The results obtained here and from our luminescence probe experiments of aqueous solutions of the Nafion polyelectrolytes (15b) suggest the possibility of a much simpler model for the ionic cluster. The luminescence probe studies clearly show that free Nafion chains in solution can engage in strong hydrophobic interactions with hydrophobic cations (e.g.  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{MV}^{2+}$ ). That is, the hydrophobic counterion can be bound to a polymer chain via a concerted hydrophobic/electrostatic interaction (15b). Given this fact, it does not seem necessary to assume that two separate ionic domain phases, with associated partition equilibria between phases, exist if a model which provides for crisscrossing of chain material through the ionic domain is allowed. The lower  $\text{Cs}^+$  diffusion coefficient observed by Yeager (18) and the lower  $D_{\text{App}}^{(n-1)+}$  values observed here would simply result from interactions of these ions, with the intruding chain material, as the ions traverse the ionic domain. It is important

to note that Eisenberg proposed exactly this type of model for the ionic cluster over a decade ago (20).

The  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  diffusion data obtained here lends support to this simpler model. Both  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  are very hydrophilic and would not be expected to partition into the hypothetical interfacial region, yet their film diffusion coefficients are about two orders of magnitude lower than the solution values. These data suggest that these complexes must traverse a rather tortuous path through the cluster. Such tortuosity could be provided by the penetration of chain material. Obviously, further work is needed if the details of ionomer morphology are to be ascertained.

Finally, during the review of this work, a paper by Buttry and Anson appeared which also dealt with mechanisms of charge transport in Nafion films (21). While the focus of our work is an interpretation of diffusion data for true ionic diffusers, the focus of Buttry and Anson's paper (21) was an interpretation of the diffusion process for counterions labeled electron hopping diffusers here (e.g.  $\text{Ru}(\text{bpy})_3^{3+/2+}$ ). Their interpretation (21) is based on Yeager's model for the ionic cluster (18) and concludes that charge transport for couples like  $\text{Ru}(\text{bpy})_3^{3+/2+}$  is much more complex than simple exchange of electrons between redox sites. Their work also points out the importance of hydrophobic interactions on the rates and mechanisms of charge transport in Nafion films (21).



### Acknowledgements

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### Figure Captions.

Figure 1. Voltammograms for electrode prepared by coating a glassy carbon rod (area=0.079 cm<sup>2</sup>) with an 1100 EW Nafion film containing  $\sim 8 \times 10^{-9}$  moles of -SO<sub>3</sub><sup>-</sup> sites. Scan rate=100 mV s<sup>-1</sup>, supporting electrolyte=0.2 M sodium trifluoroacetate (pH=3.0), potentials vs. SCE. (a) Loading in 10<sup>-3</sup> M Co(bpy)<sub>3</sub><sup>2+</sup> solution. (b) Electrode in 1a in solution containing only supporting electrolyte after three quantitative oxidation/re-reduction cycles (see text).

### Figure 2.

Chronocoulometric plots for electrode described in Figure 1b. Potential stepped from -0.2 to +0.3V vs. SCE after (a) first, (b) second and (c) third quantitative oxidation/re-reduction cycle (see text).

### Figure 3.

Chronocoulometric plots for Nafion coated electrodes ( $1.03 \times 10^{-7}$  moles -SO<sub>3</sub><sup>-</sup> sites cm<sup>-2</sup>) containing (a)  $1.61 \times 10^{-8}$  moles cm<sup>-2</sup> methylviologen. Stepped from -0.4 to -0.8 V (Vs. SCE). (b)  $1.10 \times 10^{-8}$  moles cm<sup>-2</sup> Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. Stepped from +0.05 to -0.37 V (Vs. SCE). (c)  $9.5 \times 10^{-9}$  moles cm<sup>-2</sup> Ru(bpy)<sub>3</sub><sup>3+</sup>. Stepped from +0.80 to +0.35 (Vs. MSE). (d)  $1.32 \times 10^{-8}$  moles cm<sup>-2</sup> Fe(o-phen)<sub>3</sub><sup>3+</sup>. Stepped from +1.12 to +0.60 (Vs. SCE).

Table I. Film (1100 EW) and solution diffusion data for various redox couples (units =  $\text{cm}^2 \text{s}^{-1}$ ).

Couple	Film			Solution
	$10^{10} \times D_{\text{App}}^{n+}$	$10^{10} \times D_{\text{App}}^{(n-1)+}$	$D_{\text{App}}^{n+} / D_{\text{App}}^{(n-1)+}$	
$\text{Fe}(\text{bpy})_3^{3+/2+}$	$1.0 \pm 0.3$	$1.0 \pm 0.3$	1.0	
$\text{Fe}(\text{o-phen})_3^{3+/2+}$	$0.4 \pm 0.1$	$0.4 \pm 0.1$	1.0	$0.5^a$
$\text{Ru}(\text{bpy})_3^{3+/2+}$	$1.8 \pm 0.2$	$1.7 \pm 0.2$	1.0	$0.8^b$
$\text{FA}^{2+/+}$	$3.8 \pm 0.2$	$1.3 \pm 0.2$	2.9	$0.8^c$
$\text{MV}^{2+/+}$	$18 \pm 0.4$	$4 \pm 2$	4.5	
$\text{Co}(\text{bpy})_3^{3+/2+}$	$0.2 \pm 0.1$	$0.02 \pm 0.01$	10	
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	$23 \pm 1$	$34 \pm 1$	0.7	$0.8^d$

<sup>a</sup>From I. Ruff and M. Zimonyi, *Electrochim. Acta*, 18 (1973) 515.

<sup>b</sup>From Ref. 2b.

<sup>c</sup>C. R. Martin and K. A. Dollard, unpublished data.

<sup>d</sup>From Ref. 2a.

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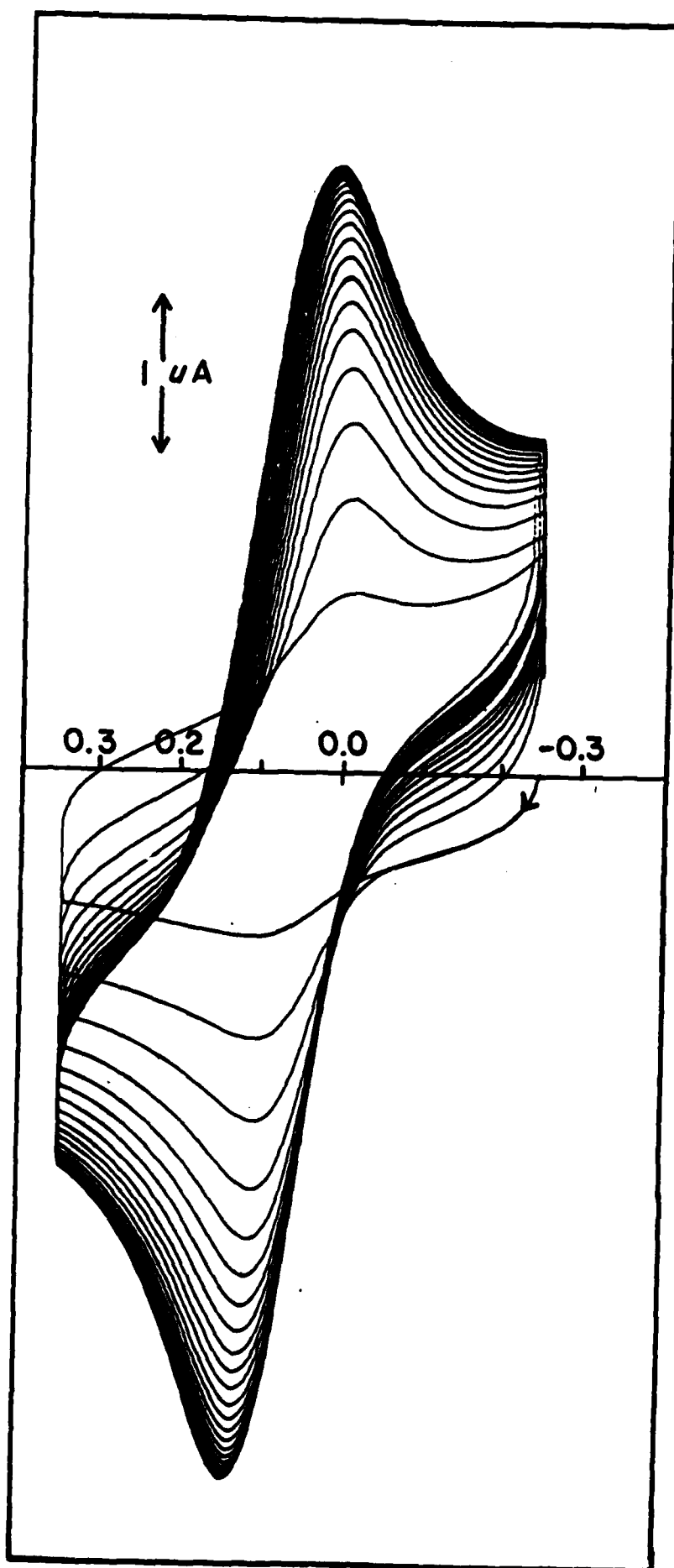


Fig. 1a

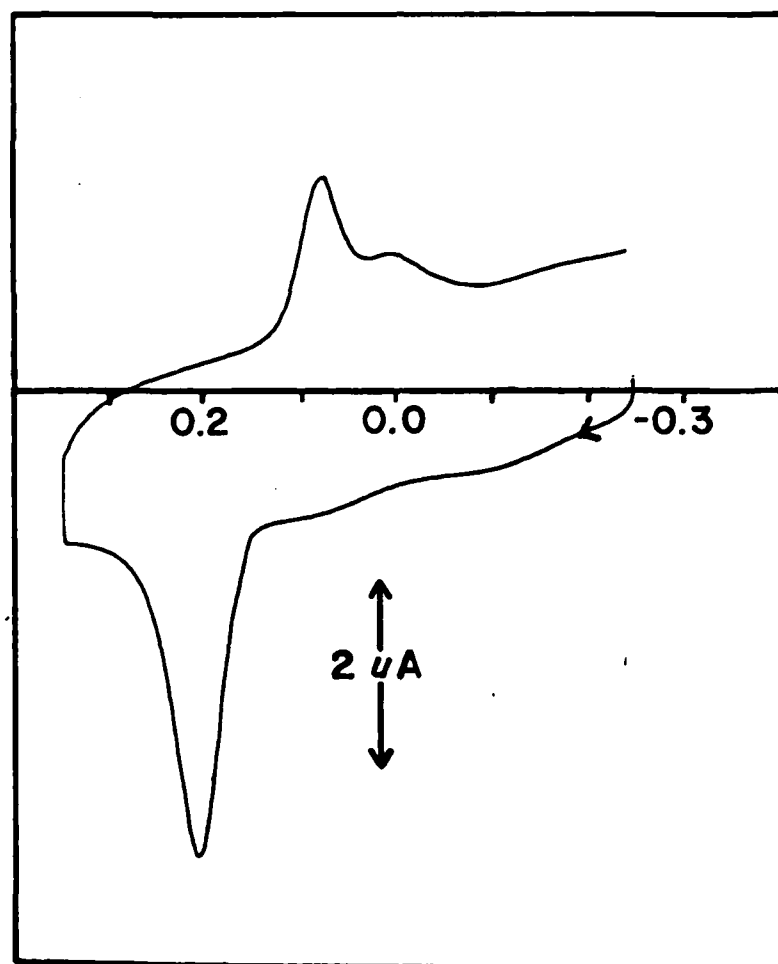


Fig. 1b

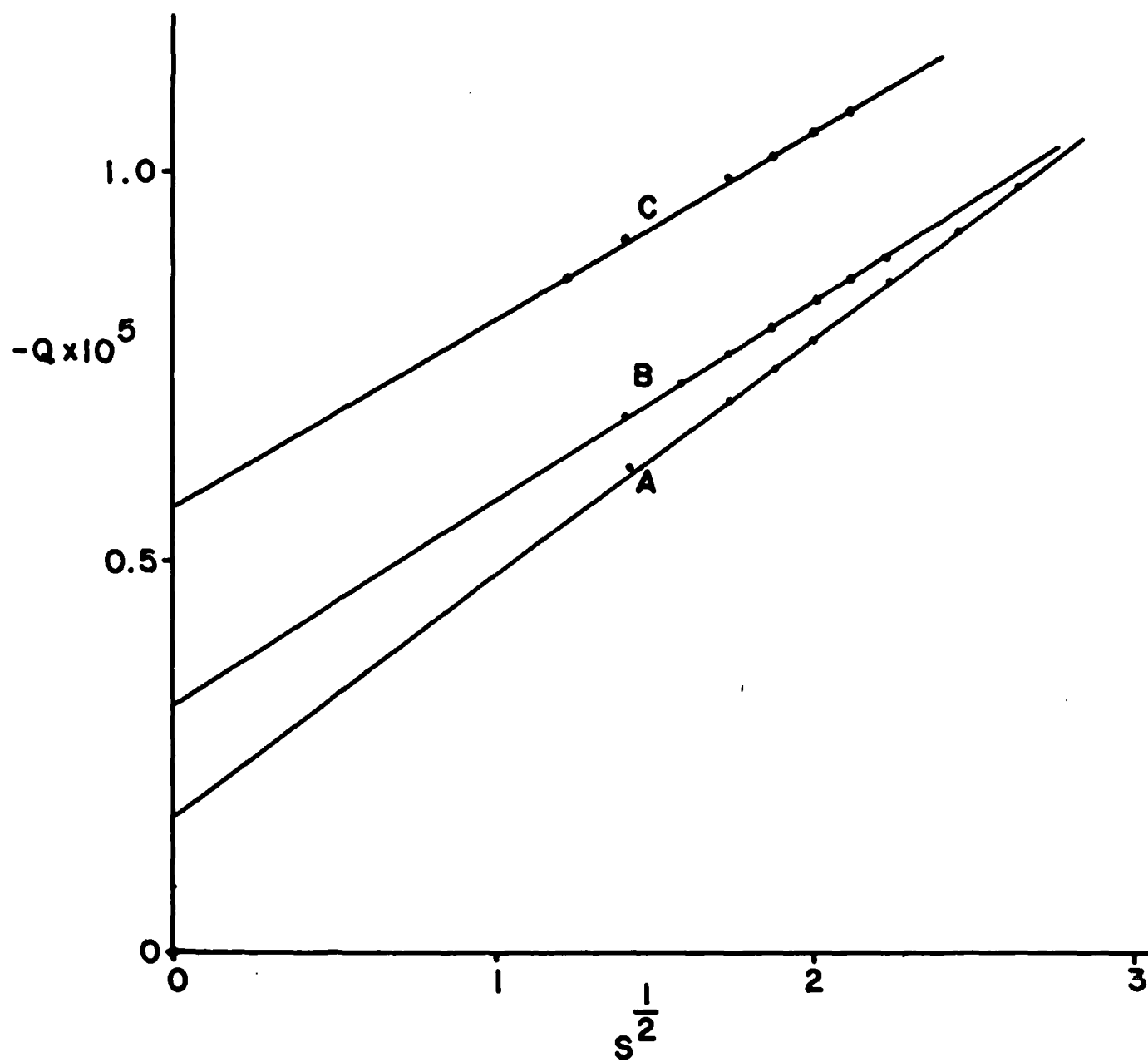
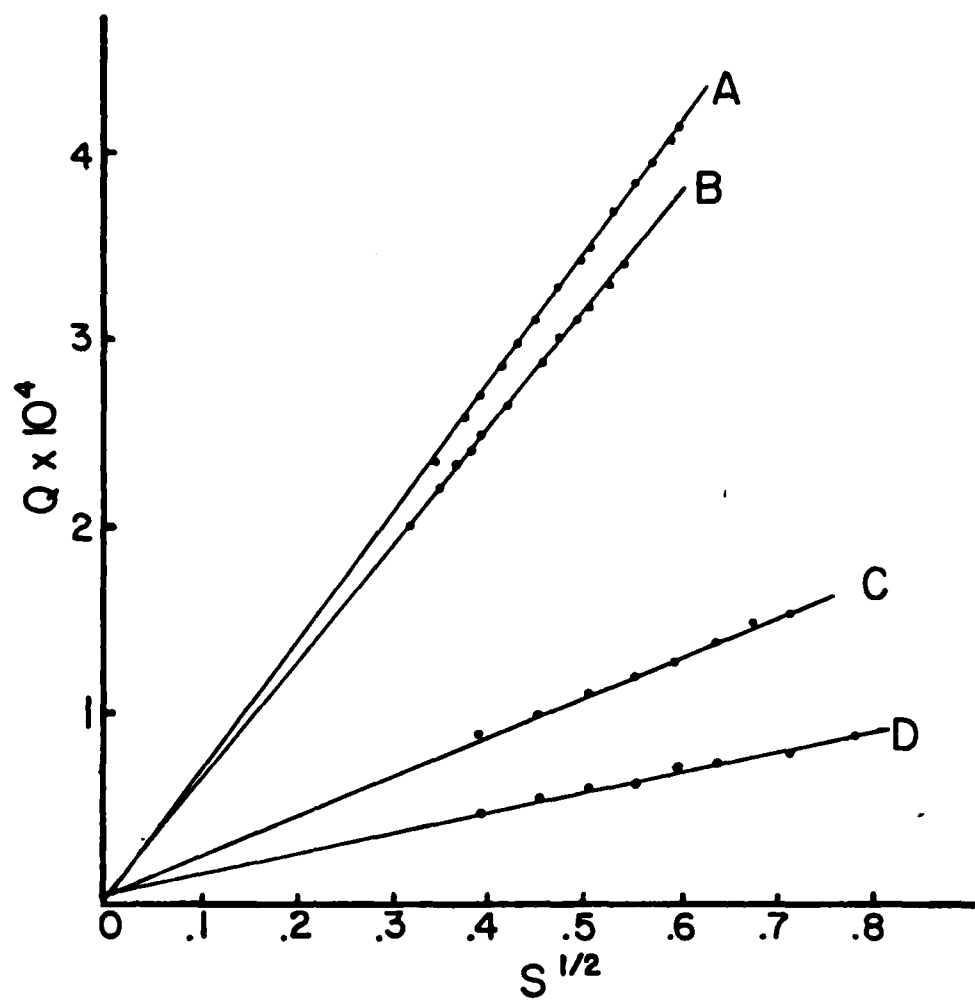


Fig. 2





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